# A DETERMINATION OF THE REACTIVITY OF SOME ESTERS OF OXALIC ACID WITH CERTAIN ORGANIC BASES.

A THESIS SUBMITTED TO THE DEPARTMENT OF CHEMISTRY AND THE FACULTY OF THE SCHOOL OF ENGINEERING OF THE UNIVERSITY OF KANSAS.

FOR

THE DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING.

BY

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## Introduction.

The purpose of this work was to determine the percentage yields of the substituted amides produced according to the following type reaction,

$$\begin{matrix}\text{COOR}\\|\\\text{COOR}\end{matrix} + 2HR' = \begin{matrix}\text{COR'}\\|\\\text{COR'}\end{matrix} + 2ROH$$

in which R may be either the methyl, ethyl, propyl, butyl, or benzyl group and HR' may be either aniline, ammonia, o-toluidine, or p-toluidine. It was desired to determine (1) the relative reactivity of the esters used, (2) the relative reactivity of the bases, and (3) the effects of varying the temperature and time of heating. It was found that some of the esters reacted to form a mono-substitution derivative according to the reaction,

$$\begin{matrix}\text{COOR}\\|\\\text{COOR}\end{matrix} + HR' = \begin{matrix}\text{COR'}\\|\\\text{COOR}\end{matrix} + ROH$$

From the literature it was learned that most of the products of these reactions had been made by the same general method but no data could be found concerning the

relative reactivity of the reagents used or of the change in rate of reaction with change in temperature.

The work naturally falls into three divisions, (1) preparation and purification of reagents, (2) preliminary experiments to determine the proper methods of carrying on the reactions, and of isolating and identifying the products, and (3) the determinations of the reactivity. The first two divisions are of course only preliminary to the third which is the important part of the work and is summarized in the tables and graphs.

The writer wishes to express his appreciation to Dr. F. B. Dains and Dr. R. Q. Brewster for their many valuable and helpful suggestions which contributed to the success of this work.

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## PREPARATION OF REAGENTS.

As many of the reagents as were available were obtained from the chemical stores at hand. Those not available were prepared by the methods outlined.

### Preparation of Normal Propyl Oxalate.

Materials.

Normal propyl alcohol ---------- 300 grams.
Fused oxalic acid ---------- 225 grams.

The reagents were mixed in a 500 c.c. round bottomed flask with reflux condenser attached and heated to 100° on a water bath for three hours. The contents of the flask were then distilled, the fraction boiling at 209° to 213° being saved. A 29 % yield was obtained.

### Preparation of Normal Butyl Oxalate.

Materials.

Normal butyl alcohol ---------- 250 grams.
Fused oxalic acid ---------- 150 grams.

The reagents were heated on a water bath at 100° for three hours and contents distilled. The fraction boiling from 239° to 243° was saved. A 30 % yield was

obtained. This was repeated using an oil bath at 115° to 125° for three hours. A 50.5 % yield was obtained.

Preparation of Benzyl Oxalate.

The literature was searched for a method of preparing this reagent and it was found that the methods described were by the action of silver oxalate on benzyl chloride. A cheaper method was desired and the following was tried.

Materials.

Benzyl alcohol ---------- 100 grams.
Fused oxalic acid ---------- 50 grams.

The reagents were mixed in a 500 c.c. round bottomed flask with reflux condenser attached and heated on an oil bath at 140° to 150° for three hours. The contents were poured into a beaker and allowed to cool. On cooling the product solidified. It was thoroughly washed with water to remove any excess of oxalic acid and finally recrystallized from alcohol and dried on a porous plate. A yield of 44 % was obtained. The reaction was repeated and the temperature allowed to rise to 160°. At this temperature the mixture frothed considerably and a heavy yellow syrupy liquid was produced. all attempts to crystallize the product from ether, alcohol, or benzene were without results.

## Preparation of Alcoholic Ammonia Solution.

Liquid ammonia was run into alcohol until a saturated solution was produced. The solution was then titrated against sulfuric acid of known concentration.

## Purification of Reagents.

The following reagents were purified by redistillation before using. The accompanying table shows the boiling point of the fractions used and the recorded boiling point of the compound.

| | Fraction used. | Recorded B. P. |
|---|---|---|
| Methyl oxalate | 160-165 | 165 |
| Ethyl oxalate | 180-184 | 184 |
| Propyl oxalate (normal) | 209-213 | 213.5 |
| Butyl oxalate ( normal ) | 239-243 | 243.5 |
| Aniline | 181-182 | 182 |
| o-Toluidine | 193-197 | 197 |

## Purification of p-Toluidine.

The p- toluidine obtained was sufficiently pure without any treatment having a melting point of 45°, the same as the recorded melting point.

## Purification of Benzyl Oxalate.

The ester was dissolved in hot alcohol, filtered, cooled and allowed to crystallize. It was then filtered, washed with water and dried on a porous plate. It melted at 80°. The recorded melting point is 81.5°.

## Preliminary Tests with Aniline.

It was desired to determine the proper method of bringing about the reaction and separating the product. For this purpose 8 inch test tubes were used. Each test tube was sealed with a cork stopper fitted with a glass tube. In each test tube was placed 1/20 mole of an ester and 1/10 mole of aniline. The tubes were then placed in a water bath and heated for one hour at 100°. A heavy precipitate was formed in the tube containing the methyl oxalate but the reaction was much less in the other tubes so they were heated in an oil bath at 125° for one hour. An appreciable precipitate was formed in each tube. The aniline was washed out with dilute hydrochloric acid and the product filtered off. It was then washed with alcohol to remove any unchanged ester and finally washed with water and dried in an electric oven. The melting point of each product was then determined. It was found that the

products from the methyl, butyl, and benzyl esters melted at 243°-245°, the melting point of oxanilid, while those from the ethyl and propyl softened at a low temperature and melted gradually as if impure. It was also noticed that the filtrates from these products formed a precipitate when the water used in washing the product ran into the alcoholic solution which had washed the excess ester from the product. From these observations it was supposed that the product contained some substance soluble to some extent in alcohol but insoluble in water. These products were then washed in hot alcohol and filtered. The precipitates when dried melted at 243°. The filtrates were diluted with water and the alcohol boiled off on a water bath. Needle like crystals formed which when dried melted at 66° from the ethyl and 91°from the propyl. The melting point of the ethyl ester of oxanilic acid is recorded as 66°-67° and the propyl ester at 92°.

From these preliminary reactions it was learned that all of the esters would react with aniline to form oxanilid,

$$\begin{matrix} COOR \\ | \\ COOR \end{matrix} + 2\ C_6H_5NH_2 = \begin{matrix} CONHC_6H_5 \\ | \\ CONHC_6H_5 \end{matrix} + 2\ ROH$$

It was also learned that one mole of aniline would react with one mole of ethyl or propyl oxalate to form the corresponding ester of oxanilic acid.

$$\begin{matrix} COOC_2H_5 \\ | \\ COOC_2H_5 \end{matrix} + C_6H_5NH_2 = \begin{matrix} CONHC_6H_5 \\ | \\ COOC_2H_5 \end{matrix} + C_2H_5OH$$

$$\begin{matrix} COOC_3H_7 \\ | \\ COOC_3H_7 \end{matrix} + C_6H_5NH_2 = \begin{matrix} CONHC_6H_5 \\ | \\ COOC_3H_7 \end{matrix} + C_3H_7OH$$

The oxanilid was found to be difficultly soluble in hot alcohol while the mono-substitution product dissolved readily in hot alcohol, slightly in cold alcohol, and could be precipitated from the alcoholic solution by diluting with water, evaporating off the alcohol and allowing to cool. The subsequent determinations of reactivity were carried out in the same manner as the preliminary tests and the products separated in the above described manner.

The Reactivity of the Esters with Aniline.

1/20 mole of the ester and 1/10 mole of aniline were used for each reaction, except benzyl oxalate. Due to the high molar weight of this ester and the limited

amount of the alcohol from which to prepare it only 1/40 mole of it was used with 1/20 mole of aniline. The following table shows the weights of reagents used. The molar weight of aniline is 93. 1/10 mole or 9.30 grams was used except with benzyl oxalate, 4.65 grams being used in this case.

| Ester | Molar wt. | Amount used. | Weight. | Aniline |
|---|---|---|---|---|
| Methyl oxalate--- | 118 | 1/20 mole | 5.9 gr. | 9.3 gr. |
| Ethyl oxalate---- | 146 | 1/20 mole | 7.3 gr. | 9.3 gr. |
| N-propyl oxalate- | 174 | 1/20 mole | 8.7 gr. | 9.3 gr. |
| N-butyl oxalate-- | 202 | 1/20 mole | 10.1 gr. | 9.3 gr. |
| Benzyl oxalate -- | 270 | 1/40 mole | 6.75 gr. | 4.65 gr. |

The solid reagents were weighed on a filter paper counter-balanced by another filter paper of equal size and weight. The liquids were weighed into tared test tubes supported on the balances in a small beaker. The liquids were pipetted into the tubes and weighed to the second decimal as nearly as possible by dropping the reagent from the pipette. The reactions were carried out in the same tubes in which the reagents were weighed. The reactivity determinations were first made by heating in a water bath at 100° for one, two, and five hours. The bath was kept full enough to surround the tubes to

the depth of the reaction mixture. The products after being separated as in the preliminary tests were dried on the filter papers in an electric oven and weighed on horn pan balances. The filter papers containing the product were counter-balanced by another filter paper of equal size and weight. The melting point of each product was determined and the percentage yield calculated. The determinations were then made using an oil bath at 125° for one hour and at 150° for one and two hours. The ethyl and propyl were found to produce a considerable yield of the mono-substitution ester and from the tables and curves may be noticed a similarity of conditions under which these products were formed. The butyl when heated for two hours at 150° gave indications of a trace of a mono-substitution product but not enough to isolate and purify sufficiently to determine its melting point. The results of these determinations are tabulated in the following tables and the percentage yields plotted on the curves. The mono-substitution ester is indicated in red type and red lines.

## Reactivity of the Esters with Aniline.

### Heated one Hour at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M.P. |
|---|---|---|---|---|---|
| Methyl | 3.26 | 12 | 27.15 | 245 | 245 |
| Ethyl | .23 | 12 | 1.90 | 245 | 245 |
| Propyl | .40 | 12 | 3.30 | 242 | 245 |
| Butyl | ------- No appreciable reaction------ | | | | |
| Benzyl | .24 | 6 | 4.00 | 243 | 245 |

### Heated two hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 5.60 | 12 | 46.60 | 241 | 245 |
| Ethyl | .44 | 12 | 3.60 | 240 | 245 |
| Propyl | .67 | 12 | 5.59 | 237 | 245 |
| | 2.76 | 10.35 | 23.00 | 88 | 92 |
| Butyl | --- No appreciable reaction --------- | | | | |
| Benzyl | .66 | 6 | 11.00 | 244 | 245 |

Heated five Hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 6.69 | 12.00 | 55.7 | 242 | 245 |
| Ethyl | 2.73 | 12.00 | 22.75 | 240 | 245 |
| | .62 | 9.65 | 6.43 | 66 | 66-67 |
| Propyl | .80 | 12.00 | 6.66 | 243 | 245 |
| | 2.85 | 10.35 | 27.55 | 91 | 92 |
| Butyl | .30 | 12.00 | 2.50 | 241 | 245 |
| Benzyl | 1.68 | 6.00 | 28.00 | 244 | 245 |

Heated one Hour at 125°.

| Ester | gr | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 5.72 | 12.00 | 47.60 | 241 | 245 |
| Ethyl | 2.18 | 12.00 | 18.15 | 239 | 245 |
| | .63 | 9.65 | 6.54 | 66 | 66-67 |
| Propyl | 1.09 | 12.00 | 9.17 | 238 | 245 |
| | 1.95 | 10.35 | 18.80 | 92 | 92 |
| Butyl | .12 | 12.00 | 1.00 | 240 | 245 |
| Benzyl | 2.13 | 6.00 | 35.50 | 243 | 245 |

Heated one Hour at 150°.

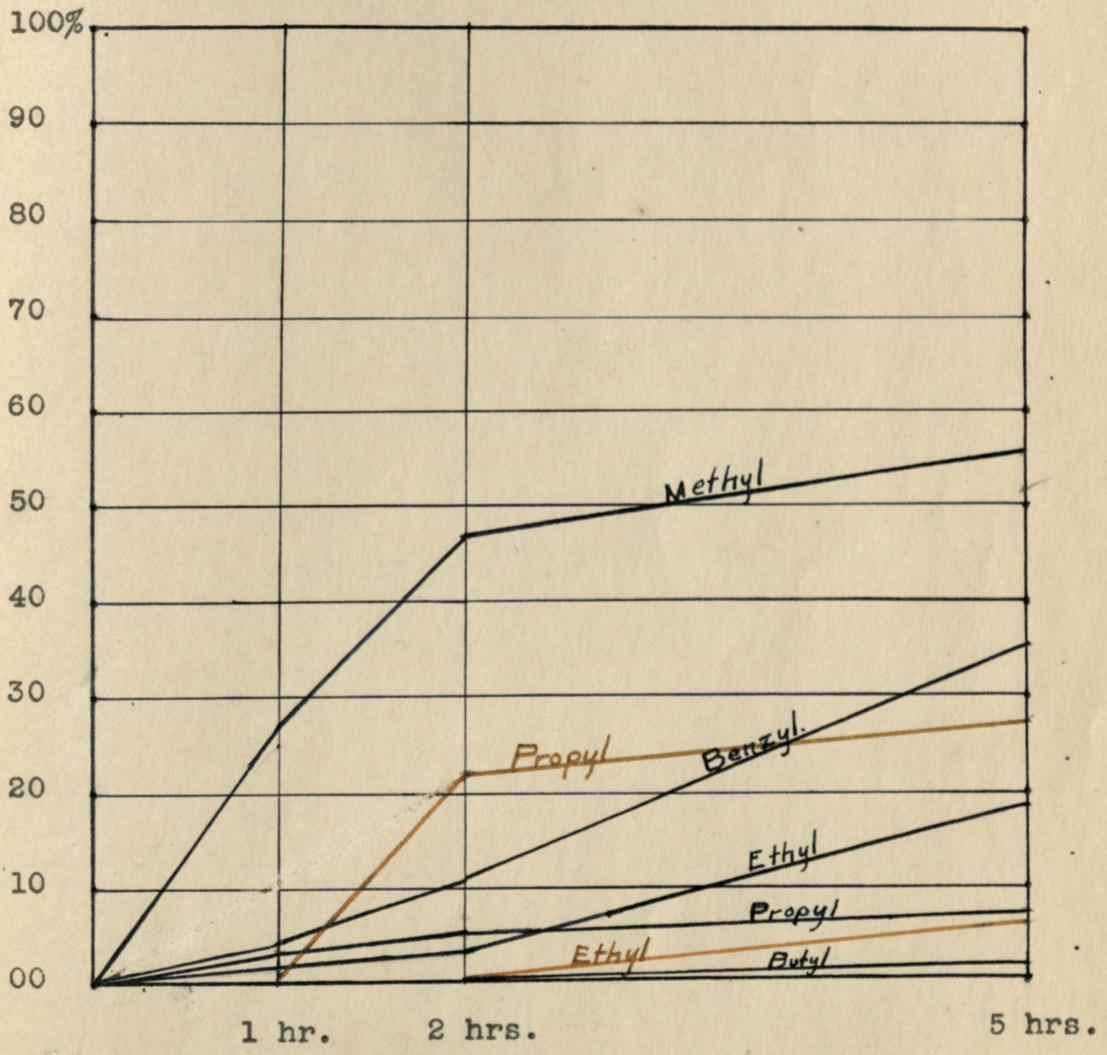
| Ester | gr. | Theo. yd. | %yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 9.65 | 12.00 | 80.50 | 245 | 245 |
| Ethyl | 2.64 | 12.00 | 22.00 | 243 | 245 |
| | 2.93 | 9.65 | 30.40 | 67 | 66-67 |
| Propyl | 1.44 | 12.00 | 12.00 | 244 | 245 |
| | 6.48 | 10.35 | 62.60 | 91 | 92 |
| Butyl | 1.15 | 12.00 | 9.59 | 238 | 245 |
| Benzyl | 3.10 | 6.00 | 51.66 | 243 | 245 |

Heated two Hours at 150°...

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 10.20 | 12.00 | 85.10 | 242 | 245 |
| Ethyl | 7.60 | 12.00 | 63.30 | 245 | 245 |
| | 2.65 | 9.65 | 27.40 | 66 | 66-67 |
| Propyl | 2.35 | 12.00 | 19.50 | 245 | 245 |
| | 7.00 | 10.35 | 67.50 | 91 | 92 |
| Butyl | 2.75 | 12.00 | 22.90 | 244 | 245 |
| Benzyl | 4.07 | 6.00 | 67.83 | 243 | 245 |

Percentage Yields with Aniline at 100°.

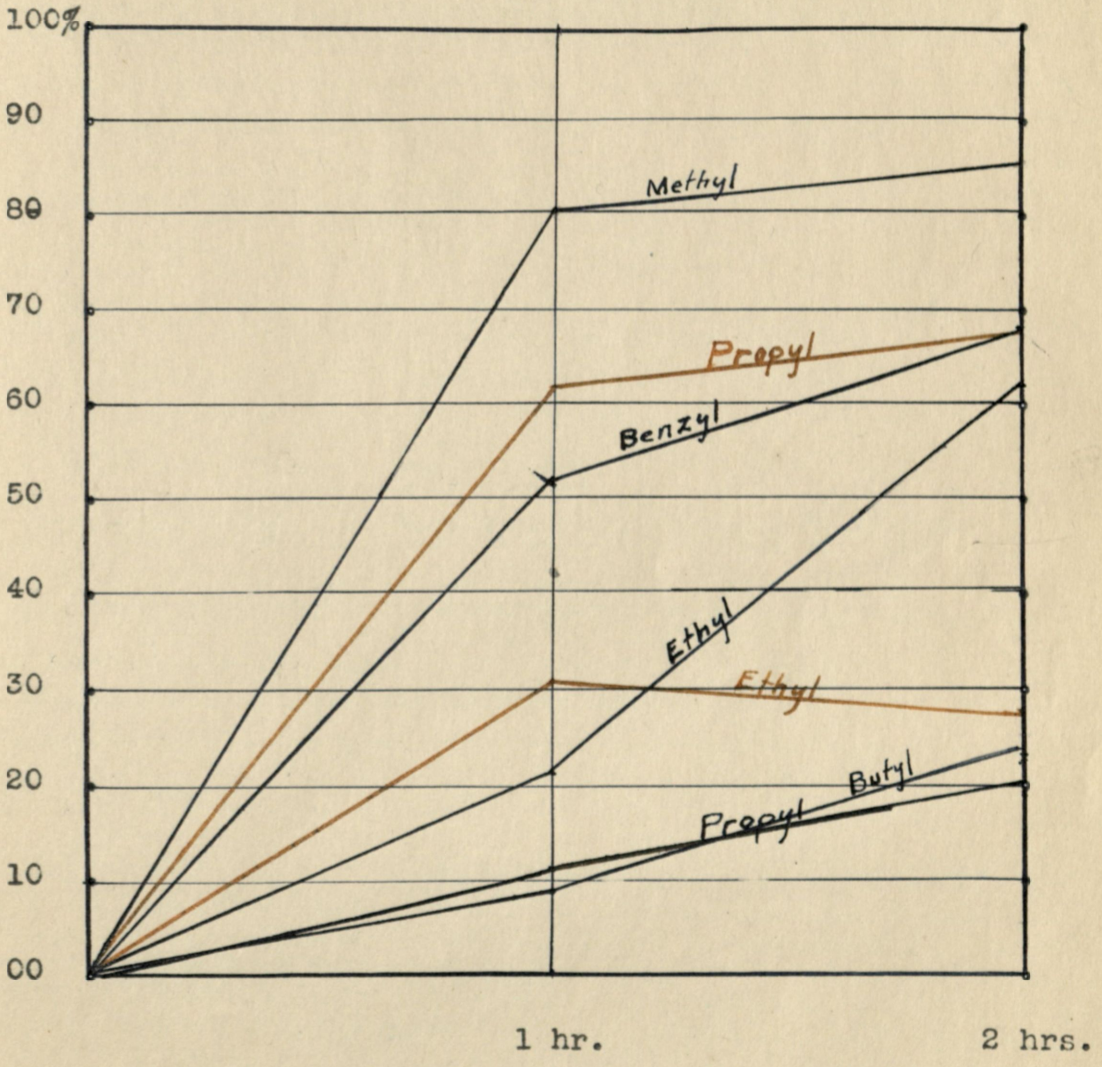
for one, two and five Hours.




Percentage yields of oxanilid.

Percentage yields of mono-substitution esters.

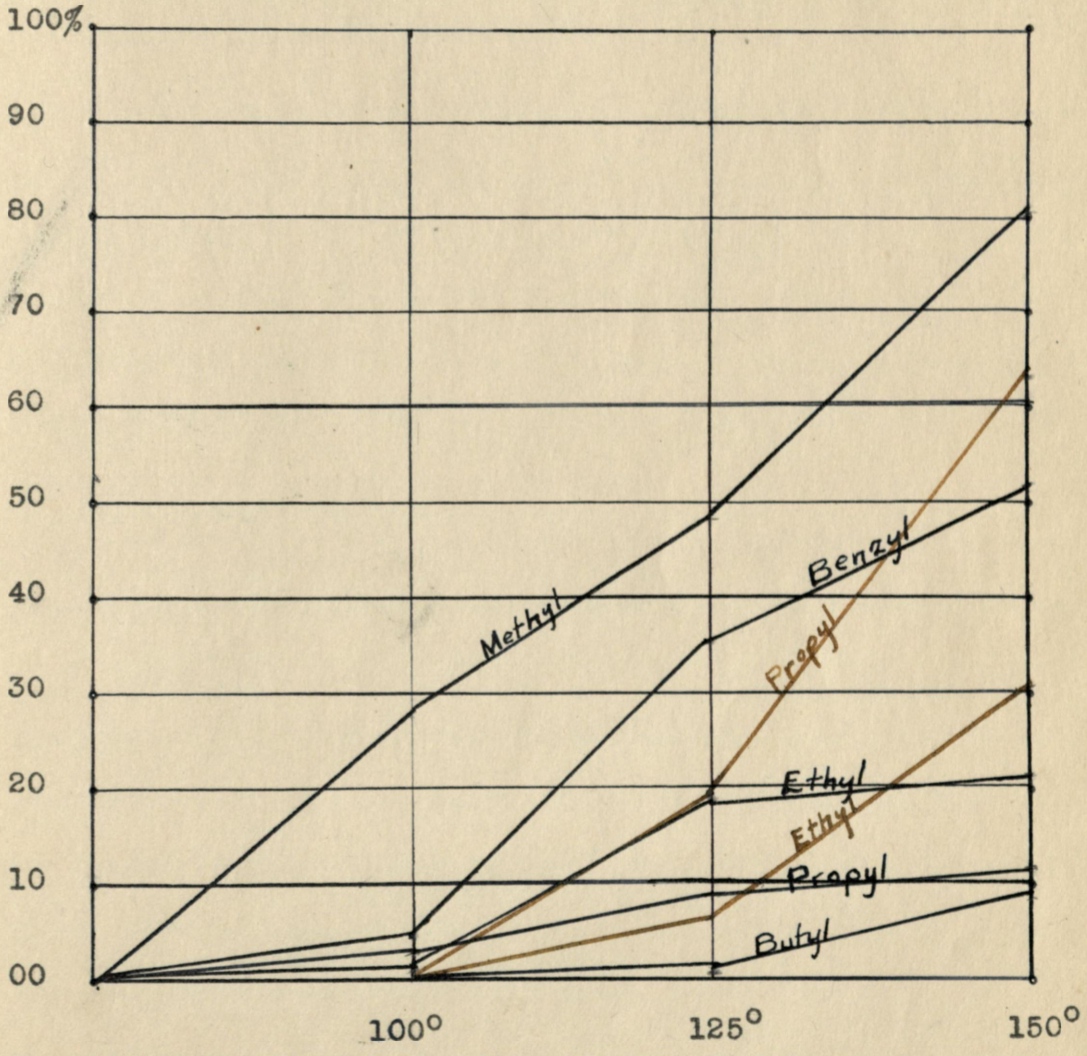
Percentage yields with Aniline at 150°
for one and two Hours.




——— Percentage yields of oxanilid.

——— Percentage yields of ester of oxanilic acid.

Percentage Yields with Aniline at 100°, 125° and 150° for one Hour.




——— Percentage yields of oxanilid.

——— Percentage yields of ester of oxanilic acid.

Reactivity of the Esters with Alcoholic Ammonia.

The same quantities of the esters were used for these reactions as in the reactions with aniline. The alcoholic ammonia solution was titrated with standard sulfuric acid and found to be approximate 4.3 normal. 40 c.c. of this was used with 1/20 mole of methyl, ethyl, propyl and butyl oxalates. 20 c.c. was diluted to 40 c.c. with alcohol and used with 1/40 mole of benzyl oxalate. These quantities contained an approximate 40 % excess of ammonia above the theoretical amount. The reagents were mixed in 250 c.c. reagent bottles and shaken in a mechanical shaker for one hour at room temperature. The products were filtered off, washed and dried. The products were weighed in the same manner as the products of the former reaction. The melting point of oxamid (418°) was too high to be determined with the apparatus at hand but the products were all heated to 275° without signs of melting and assumed to be oxamid. A quantitative amount of oxamid was produced with the ethyl, propyl, and butyl oxalates and less with the methyl and benzyl. This was considered to be due to the fact that the methyl and benzyl being solids, while the others were liquids, were more difficultly soluble in the alcoholic ammonia. It was desired to

determine if a smaller yield could be obtained in less time with a more dilute solution. For this purpose the same amount of the reagents were used and 40 c.c. more alcohol added, making a 40 % excess ammonia in 80 c.c. of alcohol. The mixture was shaken as before for 15 minutes. The reactions of the ethyl, propyl, and butyl oxalates were again found to be quantitative, while the reactions of the methyl and benzyl oxalates were somewhat less. The weights of the products obtained from the various reactions are recorded in the data on page 20 and the percentage yields plotted on page 21. In this curve the reactions are plotted uniformly during the first 15 minutes but it was believed that the initial rate of reaction was faster than is indicated by the curve. An appreciable heat of reaction was noticed as soon as the reagents were thoroughly mixed and the precipitation of the product during the first three or four minutes was very rapid. In the absence of any data in less than 15 minutes time the curve is plotted uniformly during the first 15 minutes.

## Reactivity with Alcoholic Ammonia.

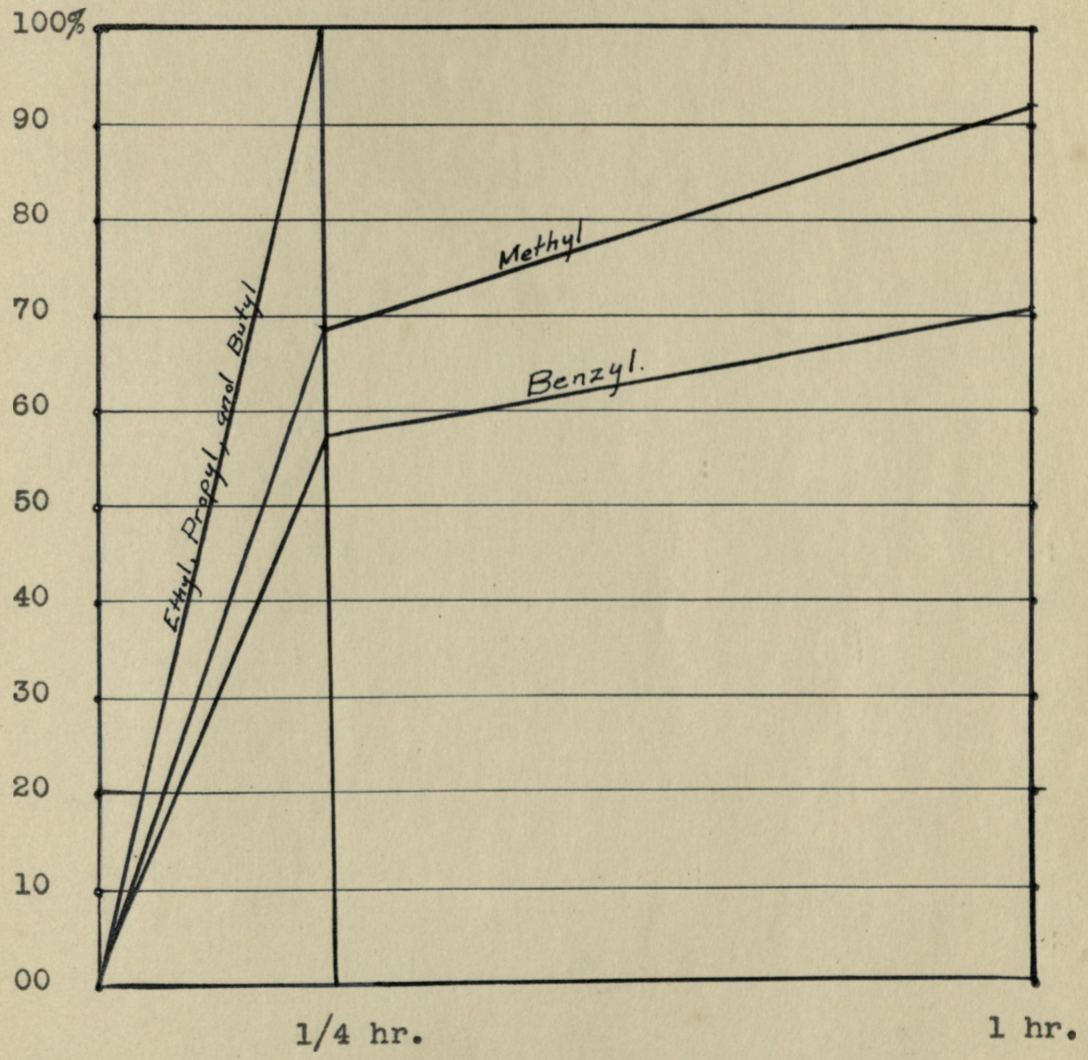
Shaken for one Hour with 40 c.c. of Alcohol containing 40 % excess Ammonia.

| Ester | grams yd. | Theo. yd. | % yd. | M.P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 4.10 | 4.40 | 93.2 | above 275° | 418° |
| Ethyl | 4.40 | 4.40 | 100.0 | " | " |
| Propyl | 4.40 | 4.40 | 100.0 | " | " |
| Butyl | 4.40 | 4.40 | 100.0 | " | " |
| Benzyl | 1.56 | 2.20 | 71.0 | " | " |

Shaken for 15 Minutes with 80 c.c. of alcohol containing 40 % excess Ammonia.

| Ester | grams yd. | Theo. yd. | % yd. | M.P. | Recorded M.P. |
|---|---|---|---|---|---|
| Methyl | 3.00 | 4.40 | 68.2 | above 275 | 418 |
| Ethyl | 4.40 | 4.40 | 100.0 | " | " |
| Propyl | 4.40 | 4.40 | 100.0 | " | " |
| Butyl | 4.40 | 4.40 | 100.0 | " | " |
| Benzyl | 1.25 | 2.20 | 56.8 | " | " |

Reactivity with Alcoholic Ammonia.




The curves represent the percentage yields of oxamide from the various esters.

Preliminary Tests with o-Toluidine.

In order to determine the products of the reactions and their properties 1/20 mole of the methyl, ethyl, propyl, and butyl oxalates (see weights given on page 10) and 1/10 mole of o-toluidine (10.7 gr.) were placed in 8 inch test tubes fitted with cork stoppers and glass tubes the same as were used for the reactions with aniline. 1/40 mole of benzyl oxalate and 1/20 mole of o-toluidine were placed in a similar tube The tubes were then heated in an oil bath for one hour at 150°. A precipitate was produced in every tube except the one containing the butyl oxalate. The products were washed with dilute hydrochloric acid to remove any unchanged o-toluidine, and with alcohol to remove the unchanged ester. The products were finally washed with water and dried in an electric oven. The products did not have a definite melting point until they were recrystallized from hot alcohol. Then they all melted at 165°. The melting point of oxaltoluid· was found to be recorded at various points between 180° and 210°.

Mixed melting points of the products from the various esters were determined and it was found a mixture of any number or of all of them melted at 165°. Fused oxalic acid was then heated with o-toluidine and a product obtained which when recrystallized and dried at 120° for two hours melted at 167°. A mixture of this product and the product from the esters melted at 166° to 167°. The product was then analyzed for nitrogen by the Kjeldahl method. The analysis calculated for oxaltoluid, $C_{16}H_{16}O_2N_2$ --- N. 10.60 %. Found 10.56, 10.44

Analytical Data.

Normality of $H_2SO_4$----- .2202 , 1 c.c. equals .003083 gr. N.

Normality of NaOH -----.2032 , 1 c.c. equals .9228 cc. acid

40.0 c. c. of acid equals 43.34 c. c. of alkali.

.5000 gram samples were used.

Titrations 40 c.c. of standard acid was used.

1. 24.55 c. c. of alkali.

2. 24.81 c. c. of alkali.

Blank 43.10 c. c. of alkali.

Reactivity with O-Toluidine.

The reagents were mixed in the same proportions as stated under the description of the preliminary tests and the percentage yields of oxaltoluid calculated according to the reaction,

$$\begin{matrix}COOR \\ | \\ COOR\end{matrix} + 2\ NH_2C_7H_7\text{-}o = \begin{matrix}CONHC_7H_7\text{-}o \\ | \\ CONHC_7H_7\text{-}o\end{matrix} + 2\ ROH$$

The determinations were made exactly as described under the reactivity with aniline, the reactivity being determined for one, two and five hours at 100°, and one hour at 125° and 150°. No mono-substitution product was identified although it was believed that traces of it existed due to the fact that the products in many cases did not melt definitely until recrystallized from alcohol. The reactions from the methyl ester were most persistent in this behavior. It might be expected that the methyl would be more likely to produce a mono-substitution product in this case than with aniline because with aniline it was more reactive and the mono-substitution product if it did exist would be more easily acted upon by the aniline to produce the di-substitution product. Also the other esters were so slightly reactive with o-toluidine that the mono-substitution product might not have appeared

until the reagents were heated to a more reactive temperature. It will be noticed from the reactions with aniline that no mono-substitution product of the ethyl ester was produced by heating for one or two hours at 100°, and that no mono-substitution product of the propyl ester was produced by heating one hour at 100°, although at higher temperatures and longer heats an appreciable amount of these products were formed. From these observations it was believed that the indefinite melting point of the product from the methyl ester before very careful purification was due to the presence of traces of a mono-substitution product which could not be isolated. The results of these determinations and calculated percentage yields are tabulated on pages 26-28 and the yields plotted on pages 29 and 30.

Heated for one Hour at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 4.40 | 13.40 | 32.80 | 165 | not reliable |
| Ethyl | ------ no apparent reaction ------ | | | | |
| Propyl | ------ " | " | " | ------ | |
| Butyl | ------ " | " | " | ------ | |
| Benzyl | Trace | | | 165 | not reliable |

Heated for two Hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 5.10 | 13.40 | 38.10 | 165 | not reliable |
| Ethyl | Trace | | | 165 | " " |
| Propyl | .15 | 13.40 | 1.12 | 165 | " " |
| Butyl | --------- no apparent reaction ----- | | | | |
| Benzyl | .40 | 6.70 | 5.97 | 167 | " " |

Heated for five Hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 6.38 | 13.40 | 47.60 | 165 | not reliable |
| Ethyl | 1.00 | 13.40 | 7.46 | 166 | " " |
| Propyl | 1.05 | 13.40 | 7.84 | 165 | " " |
| Butyl | Trace | 13.40 | | 167 | " " |
| Benzyl | .64 | 6.70 | 9.55 | 165 | " " |

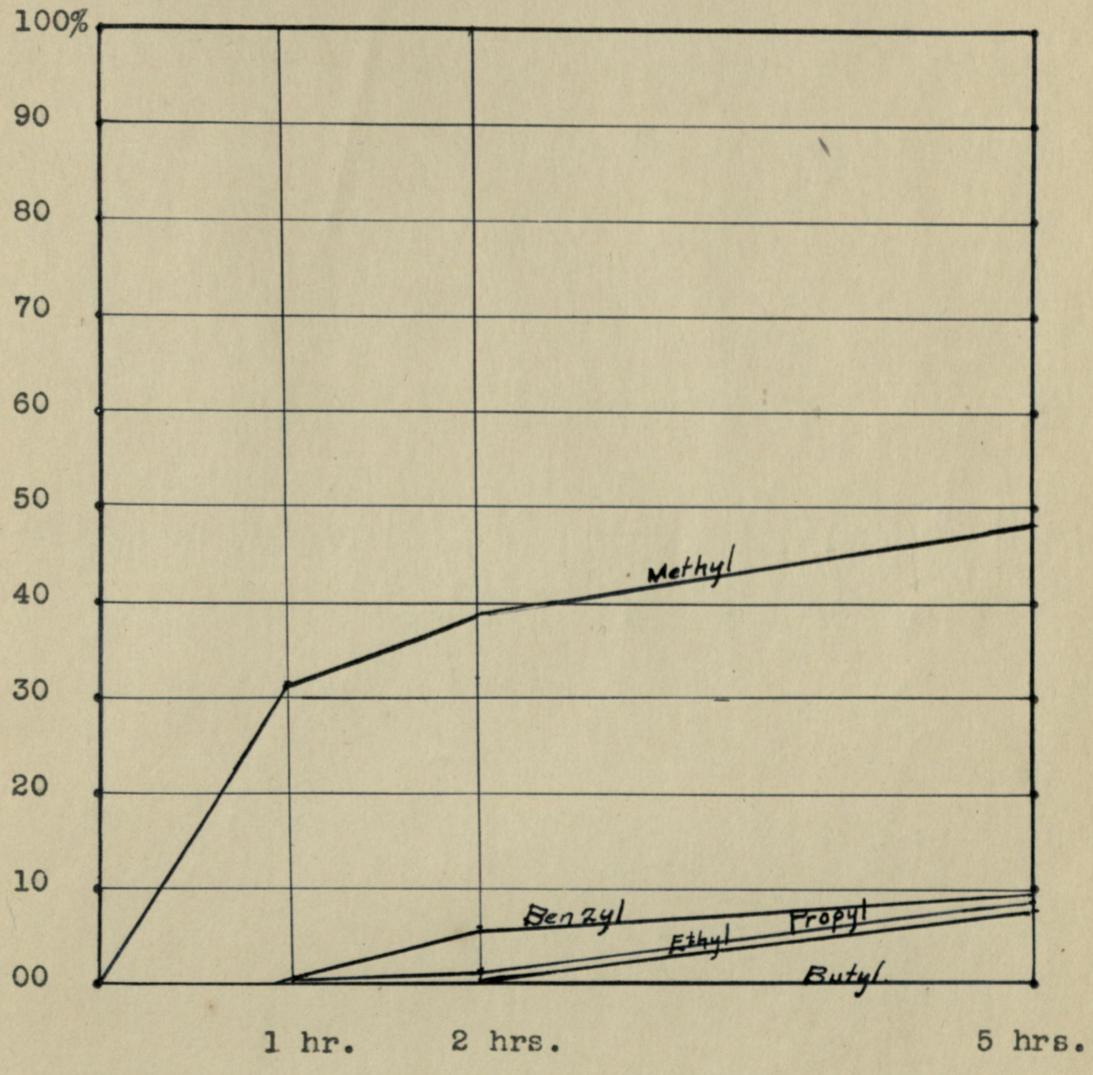
Heated for one Hour at 125°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 4.96 | 13.40 | 37.00 | 165 | not reliable |
| Ethyl | Trace | 13.40 | | 166 | " " |
| Propyl | .45 | 13.40 | 3.50 | 165 | " " |
| Butyl | --------- no apparent reaction ------- | | | | |
| Benzyl | 2.70 | 6.70 | 40.40 | 167 | " " |

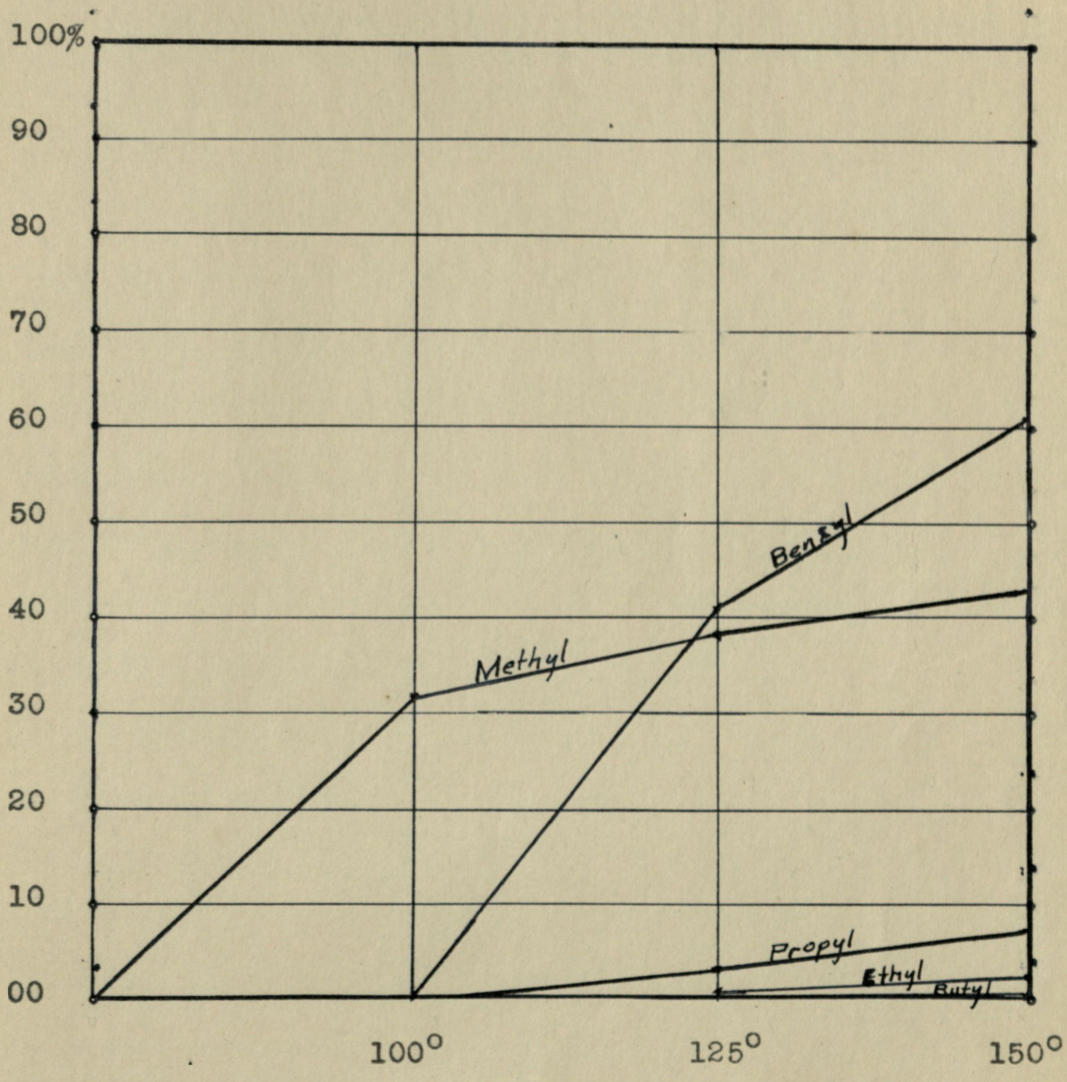
Heated for one Hour at 150°.

| Ester | gr. | Theo. yd. | % yd. | M.P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 5.82 | 13.40 | 43.40 | 165 | not reliable |
| Ethyl | .28 | 13.40 | 2.08 | 166 | " " |
| Propyl | .90 | 13.40 | 6.71 | 165 | " " |
| Butyl | -------- no apparent reaction ---- | | | | |
| Benzyl | 4.15 | 6.70 | 62.00 | 165 | " " |

Percentage yields with o-Toluidine at 100°
for one, two, and five Hours.



Percentage yields with o-Toluidine at 100°, 125°, and 150° for one Hour.



## Preliminary Tests with p-Toluidine.

The preliminary tests with p- toluidine were made with the same quantities of reagents as were used in the determinations with o-toluidine and were to be used for the subsequent determinations of the reactivity of p-toluidine. The tubes containing the mixtures were heated in an oil bath at 150° for one hour. The products were then washed with hydrochloric acid and alcohol in the usual way, and lastly with water. It was noticed that a precipitate formed when water was added to the alcoholic washings of the products from the methyl, ethyl, propyl, and butyl oxalates. These products were then thoroughly washed with hot alcohol, the filtrated diluted with water and the alcohol evaporated off. It was observed that by evaporating off the alcohol the product became tarry and difficult to crystallize. The attempttto evaporate off the alcohol was therefore abandoned and the filtrates diluted until further dilution failed to precipitate more of the product. The solution was then allowed to stand several minutes and filtered and washed with water. When the products were dried and the melting points determined it was found that products insoluble in alcohol all melted at 257° to 263°. The melting point of oxatoluid is record-

ed at 263°.[1] The product recovered from the alcoholic washings of the methyl reaction melted at 142°. No recorded melting point could be found for the methyl ester of oxatoluidic acid. The corresponding product from the ethyl ester melted at 66°, the same as the recorded melting point of the ethyl ester of oxatoluidic acid. The corresponding product from the propyl ester melted at 87°, and from the butyl at 79°. No data could be found concerning the propyl or butyl esters. Since the melting point of the alcoholic soluble product from the ethyl oxalate was the same as the recorded melting point of the ethyl ester of oxatoluidic acid it was believed that all the products recovered from the alcoholic washings were the corresponding esters of oxatoluidic acid. To confirm this belief the products were analyzed for nitrogen by the Kjeldahl method.

The calculated nitrogen content for the methyl ester of oxatoluidid, $C_{10}H_{11}O_3N$ is 7.25 %. Found 7.40, and 7.24

Analytical Data.

Normality of $H_2SO_4$ ------ .2202

Normality of NaOH ------ .2032

.5000 gram samples were used.

Titrations 40.0 c. c. of standard acid was used

1. 30.10 c. c. of alkali.

2. 30.35 c. c. of alkali.

Blank 43.10 c.c. of alkali.

The calculated nitrogen for the propyl ester of oxatoluidic acid, $C_{12}H_{15}O_3N$ , is 6.33 % . The found values were 6.16, and 6.26 %

Analytical Data.

Normality of $H_2SO_4$ -------- .2202

Normality of NaOH -------- .2032

.5000 gram samples were used.

Titrations 40.0 c.c. of standard acid were used.

1. 32.31 c.c. of alkali.

2. 32.15 c.c. of alkali.

Blank 43.10 c.c. of alkali.

The calculated nitrogen for the butyl ester of oxatoluidic acid, $C_{13}H_{17}O_3N$, is 5.95 %. The found values were 5.68 and 5.73 %.

Analytical Data.

Normality of $H_2SO_4$ -------- .2202

Normality of NaOH -------- .2032

.5000 gram samples were used.

Titrations 40.0 c.c. of standard acid was used.

1. 33.05 c.c. of alkali.

2. 32.91 c.c. of alkali.

Blank 43.10 c.c. of alkali.

From these preliminary determinations it was learned that the methyl, ethyl, propyl, and butyl oxalates reacted with p-toluidine to form both oxatoluid and the esters of oxatoluidic acid. It was learned that benzyl oxalate reacted with p-toluidine to form oxatoluid. The mono-substitution esters were found to be readily soluble in hot alcohol and the oxatoluid only slightly so.

Reactivity with p-Toluidine.

The same quantities of reagents were used as in the determinations with o-toluidine. The determinations were made at 100° for one, two, and five hours and at 125° and 150° for one hour. The reagents and products were weighed in the same manner as in the previous determinations. The mono-substitutions esters were dissolved from the oxatoluid with warm alcohol and precipitated by diluting with water. The results of these determinations are tabulated on pages 35 to 37 and the percentage yields plotted on pages 38 and 39.

## Reactivity of the Esters with p-Toluidine.

### Heated for one Hour at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 3.16 | 13.40 | 23.59 | 261 | 263 |
| | .94 | 9.65 | 9.74 | 142 | No data |
| Ethyl | .25 | 13.40 | 1.86 | 263 | 263 |
| | 1.92 | 10.35 | 18.55 | 66 | 66 |
| Propyl | .31 | 13.40 | 2.31 | 262 | 263 |
| | .69 | 11.05 | 6.24 | 87 | No data |
| Butyl | -------- Reaction too slight to determine. | | | | |
| Benzyl | .43 | 6.70 | 6.41 | 262 | 263 |

### Heated for two Hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 3.25 | 13.40 | 24.22 | 260 | 263 |
| | 2.65 | 9.65 | 27.40 | 140 | No data |
| Ethyl | .55 | 13.40 | 4.11 | 262 | 263 |
| | 3.22 | 10.35 | 31.10 | 65 | 66 |
| Propyl | .44 | 13.40 | 3.28 | 261 | 263 |
| | 4.32 | 11.05 | 39.10 | 85 | No data |
| Butyl | ----Reaction too slight to determine--- | | | | |
| Benzyl | 1.08 | 6.70 | 16.13 | 263 | 263 |

Heated for five Hours at 100°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 3.42 | 13.40 | 25.50 | 260 | 263 |
| | 2.90 | 9.65 | 30.80 | 140 | No data |
| Ethyl | 3.44 | 13.40 | 25.64 | 262 | 263 |
| | 1.64 | 10.35 | 15.85 | 66 | 66 |
| Propyl | 4.32 | 13.40 | 32.10 | 259 | 263 |
| | 2.66 | 11.05 | 24.10 | 86 | No data |
| Butyl | 4.36 | 13.40 | 32.50 | 260 | 263 |
| | 3.42 | 11.75 | 29.10 | 79 | No data. |
| Benzyl | 1.94 | 6.70 | 28.96 | 261 | 263 |

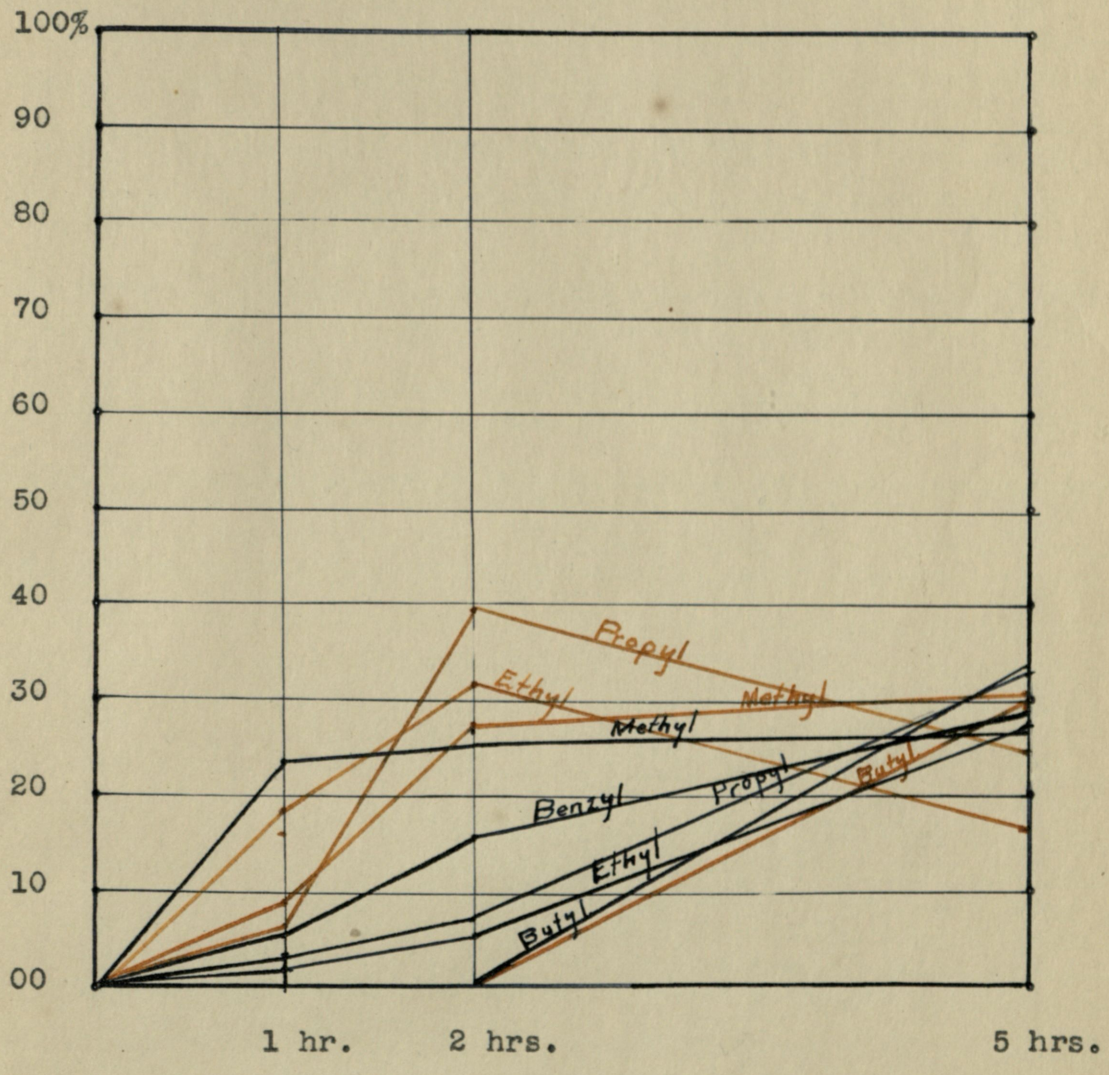
Heated for one hour at 125°.

| Ester | gr. | Theo. yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 4.10 | 13.40 | 30.60 | 258 | 263 |
| | 1.25 | 9.65 | 12.95 | 142 | No data |
| Ethyl | 1.60 | 13.40 | 11.92 | 262 | 263 |
| | 1.40 | 10.35 | 13.50 | 66 | 66 |
| Propyl | 2.20 | 13.40 | 16.40 | 263 | 263 |
| | 2.60 | 11.05 | 23.50 | 87 | No data |
| Butyl | .20 | 13.40 | 1.49 | 259 | 263 |
| Benzyl | 2.60 | 6.70 | 38.80 | 261 | 263 |

Heated for one Hour at 150°.

| Ester | gr. | Theo.yd. | % yd. | M. P. | Recorded M. P. |
|---|---|---|---|---|---|
| Methyl | 5.30 | 13.40 | 39.58 | 258 | 263 |
| | .93 | 9.65 | 9.54 | 142 | No data |
| Ethyl | 7.10 | 13.40 | 53.00 | 261 | 263 |
| | 1.85 | 10.35 | 17.84 | 66 | 66 |
| Propyl | 5.00 | 13.40 | 37.26 | 260 | 263 |
| | 2.40 | 11.05 | 21.75 | 87 | No data |
| Butyl | 4.15 | 13.40 | 31.00 | 263 | 263 |
| | 2.10 | 11.75 | 21.70 | 79 | No data |
| Benzyl | 3.10 | 6.70 | 46.32 | 259 | 263 |

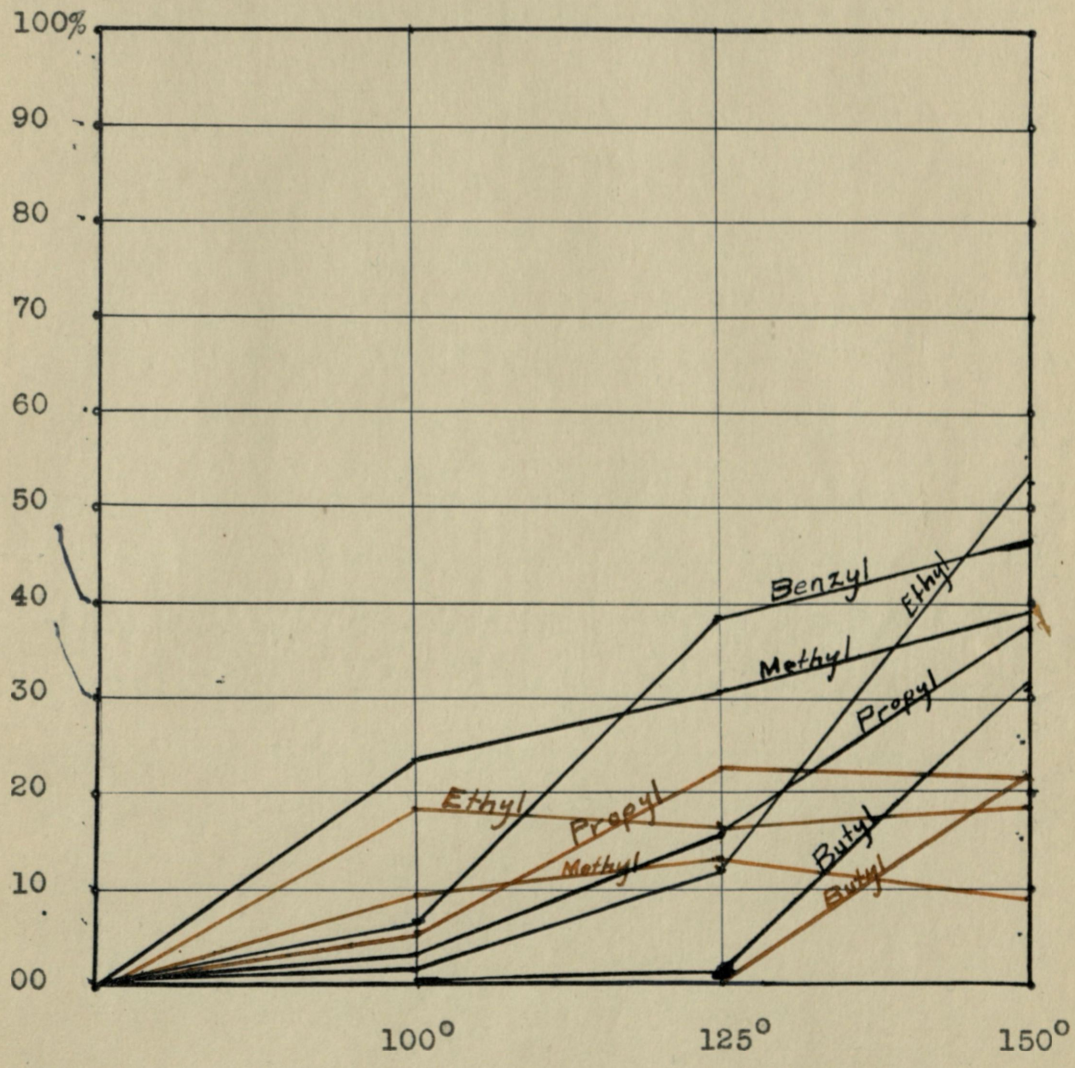
Percentage yields with p-Toluidine at 100°
for one, two, and five Hours.




di-substitution product.

mono-substitution product.

Percentage yields with p-Toluidine at 100°, 125°, and 150° for one Hour.




——————— di-substitution product.

——————— mono-substitution product.

## Conclusion..

A study of the various reactivity curves throughout this paper reveals a number of interesting things. For the purpose of comparing (1) the relative reactivity of the esters, (2) the relative reactivity of the bases, and (3) the effects of varying the temperature and time of heating, the percentage yields of all the reactions are tabulated on pages 43 to 45, and the percentage yields of the esters with the three aromatic amines for one hour at 125° are plotted on page 46.

From this data it was observed that as a rule the methyl ester was the most reactive and the benzyl second in reactivity. Exceptions to this rule occur in the reactions with ammonia and some reactions with p-toluidine. This was considered to be due to the fact that these esters being solids were less readily dissolved in these particular bases than were the liquid esters. The p-toluidine being a solid made its solution with the solid esters rather difficult. The ethyl and propyl esters were found to be very similar in reactivity, while the butyl ester was found to be generally the least reactive. However when heated with p-toluidine for five hours at 100° there is little difference in the reactivity of the esters, the butyl being slightly the most reactive.

It was found that ammonia was the most reactive of the bases used, and that generally the reactivity of the aromatic amines was in the order of their basicity, p-toluidine, aniline and o-toluidine. Exceptions to this occur in certain reactions with the methyl and benzyl esters as stated above.

It was quite frequently found that the reaction was considerably greater the second hour than it was the first which led to the belief that auto-catalysis occurs. Very often this increase in reactivity was accompanied by the formation of the mono-substitution ester. It was found that increasing the temperature caused a marked increase in reactivity. It was noticed that the greatest increase in reactivity with increase in temperature occurred in some cases between 100° and 125°, while in other cases it occurred between 125° and 150°. Therefore no general rule can be applied to this particular phase of the subject.

The production of the mono-substitution esters was an extremely interesting part of this work. Due to observations already mentioned it was believed that traces of the mono-substitution esters existed in a number of reactions from which it was impossible to isolate enough to identify. The equilibrium between the mono-substitution and di-substitution products was found to vary with the

conditions of the experiment. It was noticed in a number of cases the di-substitution product occured earlier in the reaction than did the mono-substitution product. No data could be obtained to indicate whether the mono-substitution product reacted more readily to form the di-substitution product in the early stages of the reaction than in later stages, or if the mono-substitution product was not produced until the later stage.

Table of Results.

% yields.

1 Hour at 100°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Analine | 27.15 | 1.90 | 3.30 | 0 | 4.00 |
| o-Toluidine | 4.40 | 0 | 0 | 0 | Trace |
| p-Toluidine | 23.59 | 1.86 | 2.31 | 0 | 6.41 |
| | 9.74 | 18.55 | 6.24 | | |

2 Hours at 100°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Analine | 46.60 | 3.60 | 5.59 | 0 | 11 |
| | | | 23.00 | | |
| o-Toluidine | 38.10 | 0 | 1.12 | 0 | 5.97 |
| p-Toluidine | 24.22 | 4.11 | 3.28 | 0 | 16.13 |
| | 27.40 | 31.10 | 39.10 | | |

5 hours at 100°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Analine | 55.70 | 22.75 | 6.66 | 2.50 | 28.00 |
| | | 6.43 | 27.55 | | |
| o-Toluidine | 47.60 | 7.46 | 7.84 | 0 | 9.55 |
| p-Toluidine | 25.50 | 25.64 | 32.10 | 32.50 | 28.96 |
| | 30.80 | 15.85 | 24.10 | 29.10 | |

1 hour at 125°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Aniline | 47.60 | 18.15 | 9.17 | 1.00 | 35.50 |
| | | 6.54 | 18.80 | | |
| o-Toluidine | 37.00 | 0 | 3.50 | 0 | 40.40 |
| p-Toluidine | 30.60 | 11.92 | 16.40 | 1.49 | 38.80 |
| | 12.95 | 13.50 | 23.50 | | |

1 hour at 150°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Aniline | 80.50 | 22.00 | 12.00 | 9.59 | 51.66 |
| | | 30.40 | 62.60 | | |
| o-Toluidine | 43.40 | 2.08 | 6.71 | 0 | 62.00 |
| p-Toluidine | 39.58 | 52.00 | 37.26 | 31.00 | 46.32 |
| | 9.54 | 17.84 | 21.75 | 21.70 | |

2 hours at 150°.

| Bases | Esters | | | | |
|---|---|---|---|---|---|
| | Methyl | Ethyl | Propyl | Butyl | Benzyl |
| Aniline | 85.10 | 63.30 | 19.50 | 22.90 | 67.83 |
| | | 27.40 | 67.50 | | |

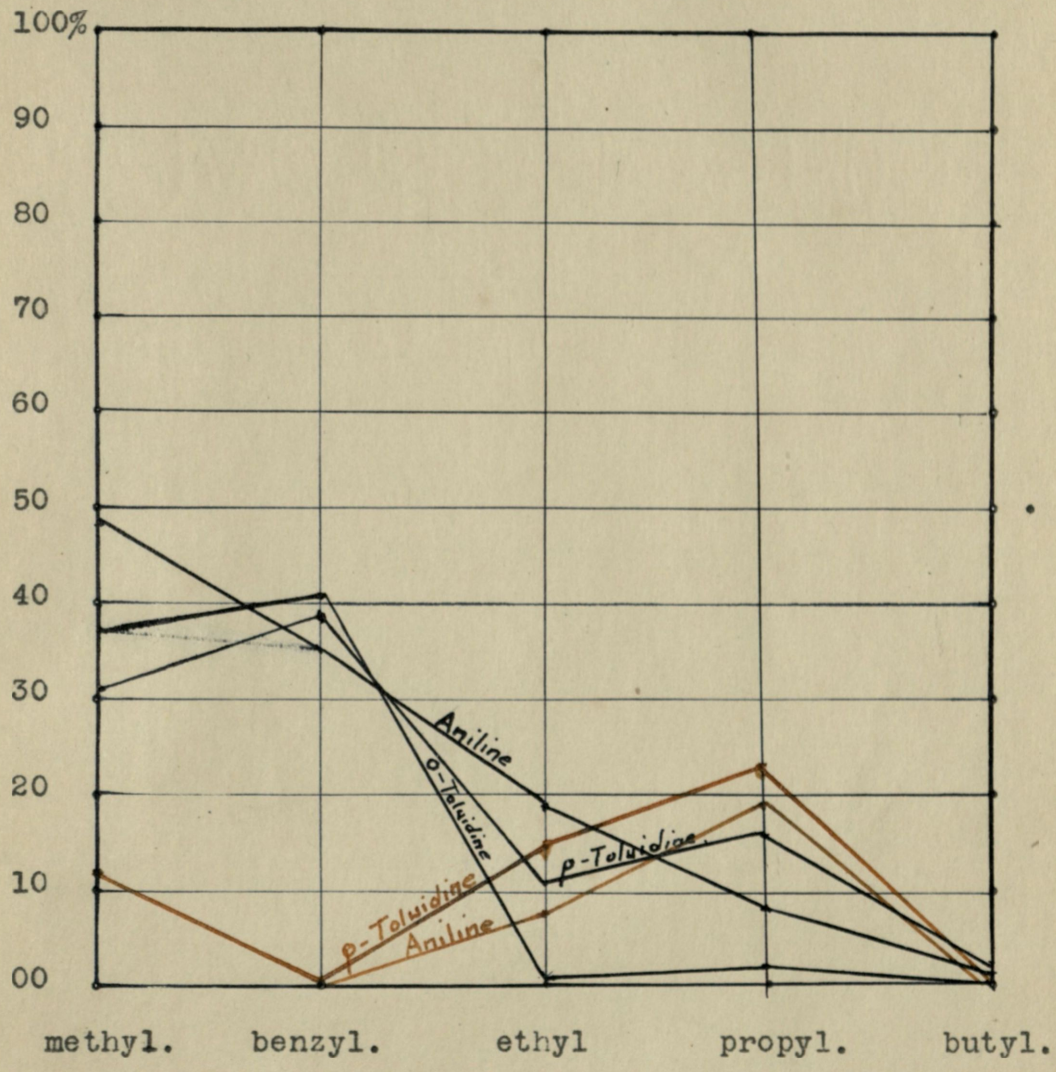
## Reactivity with Ammonia

### Esters

| Time | Methyl | Ethyl | Propyl | Butyl | Benzyl |
|---|---|---|---|---|---|
| 15 min. | 68.20 | 100 | 100 | 100 | 56.80 |
| 1 hr. | 93.2 | 100 | 100 | 100 | 71.00 |

Relative Reactivity of the Esters

and Bases at 125° for one Hour.




di-substitution product.

mono-substitution product.